

Viscosity anomaly in core-softened liquids

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(Dated: March 20, 2013)

The present article presents a molecular dynamics study of several anomalies of core-softened systems. It is well known that many core-softened liquids demonstrate diffusion anomaly. Usual intuition relates the diffusion coefficient to shear viscosity via Stokes-Einstein relation. However, it can break down at low temperature. In this respect it is important to see if viscosity also demonstrates anomalous behavior.

PACS numbers: 61.20.Gy, 61.20.Ne, 64.60.Kw

INTRODUCTION

It is well known that some liquids (for example, water, silica, silicon, carbon, and phosphorus) show an anomalous behavior [1–6]: their phase diagrams have regions where a thermal expansion coefficient is negative (density anomaly), self-diffusivity increases upon compression (diffusion anomaly), and the structural order of the system decreases with increasing pressure (structural anomaly) [3, 4]. A number of studies demonstrates water-like anomalies in fluids that interact through spherically symmetric potentials (see, for example, [7, 17, 18] and references therein). Many of these studies report the appearance of diffusion anomaly in different systems. However, the diffusion coefficient is closely related to shear viscosity of liquid therefore one can expect that the shear viscosity also demonstrates some kind of anomalous behavior.

Although many studies of core-softened systems report the diffusivity calculations there is a lack of studies which calculate shear viscosity. This can be related to the fact that viscosity is much harder to compute in simulation. So the usual intuition is applied: the viscosity can be extracted from the diffusion coefficient by Stokes-Einstein (SE) relation [8]. However, it was recently found that SE relation can be violated at low temperatures [9, 10]. This case the usual intuition can fail to predict the viscosity behavior correctly. In this respect it is important to monitor both the diffusion coefficient and shear viscosity of core-softened liquids at low temperatures to see their behavior in the regions of anomalous behavior.

The goal of the present article is to investigate the behavior of shear viscosity of core-softened fluids at low temperatures, to see if their shear viscosity demonstrates anomalous behavior and if so to find the relation between the viscosity anomaly region and the regions of other anomalies.

SYSTEMS AND METHODS

Two systems are studied in the present work. The first one is a core-softened system introduced by de Oliveira et al [11]. This system is described by the Lennard-Jones potential with Gaussian well (LJG):

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + a\varepsilon \cdot \exp \left(-\frac{1}{c^2} \left(\frac{r-r_0}{\sigma_0} \right)^2 \right), \quad (1)$$

with $a = 5.0$, $r_0/\sigma = 0.7$ and $c = 1.0$. The diffusivity of this system was studied in several papers [11–15]. Note that the parameters of the potential are chosen in such a way that the effect of attraction becomes negligibly small and one can consider this system as a purely repulsive core-softened one.

The second system studied in this work is Soft Repulsive Shoulder System (SRSS) introduced in the work [16]. The potential of this system has form:

$$U(r) = \varepsilon \left(\frac{\sigma}{r} \right)^{14} + \frac{1}{2} \varepsilon \cdot [1 - \tanh(k_0 \{r - \sigma_1\})], \quad (2)$$

where σ is "hard"-core diameter, $\sigma_1 = 1.35$ is soft-core diameter and $k_0 = 10.0$. In Ref. [17] it was shown that this system demonstrates anomalous behavior. Our later publications gave detailed study of diffusion, density and structural anomalies in this system [18].

It is well known that there is a close link between diffusion coefficient and shear viscosity of liquids. Viscosity is a quantity which is usually measured in experiments. However, due to the technical problems the simulation of shear viscosity represented in the literature is very poor. One of the goals of this article is to study the behavior of viscosity of the two model liquids described above. Taking into account that the diffusion coefficient demonstrates anomalous behavior for these systems we are interesting to see if the viscosity also demonstrates some anomalies.

In order to study the transport coefficients of the systems we used Molecular Dynamics method. In both cases a system of $N = 1000$ particles was simulated. The equations of motion were integrated by velocity Verlet algorithm. In case of LJG system the time step was set to $dt = 0.001$, the equilibration period was $3.5 \cdot 10^6$ steps and the production period $1 \cdot 10^6$ steps. In the case of SRSS the equilibration the time step was $dt = 0.0005$, the equilibration period was $3.5 \cdot 10^6$ and the production run was $0.5 \cdot 10^6$ steps. The cut-off radius was set 3.5 for LJG system and 2.2 for SRSS. Velocity rescaling was applied during equilibration, the production corresponded to NVE ensemble. Shear viscosity is difficult to measure in simulation because of large fluctuations of shear stress function. In order to improve the precision of the data we increased the equilibration time in anomalous region up to $7.5 \cdot 10^6$ and the production time up to $1.5 \cdot 10^6$ for some simulations.

In order to get good statistics on the transport properties of the systems many data points were simulated. In the case of LJG system the data points were chosen in the density interval from $\rho = 0.05$ till $\rho = 0.3$ with step $\delta\rho = 0.01$ along several isotherms. The following isotherms were considered: $T = 0.15; 0.2; 0.25; 0.3; 0.4; 0.5; 1.0$. In order to see the anomalous region better we also simulated the isotherms $T = 0.17$ and 0.23 for the densities from $\rho = 0.08$ up to 0.18 with step 0.01 .

In case of SRSS we used the densities from $\rho = 0.3$ up to $\rho = 0.8$ with step $\delta\rho = 0.05$ and temperatures $T = 0.2; 0.25; 0.3; 0.35; 0.4; 0.5; 0.7$ and 1.0 .

The diffusion coefficients were computed via Einstein relation and shear viscosity by integration of shear stress autocorrelation function.

RESULTS AND DISCUSSION

Lennard-Jones - Gauss system

As it was mentioned in the introduction the viscosity anomaly in LJG system was already reported in Ref. [19]. Here we make a more detailed simulation study of this anomaly. Our goal is to see the location of the anomaly in $\rho - T$ plane and its relation with other anomalies, such as diffusion anomaly, density anomaly and structural anomaly.

Figs. 1 shows the viscosity along several isotherms for LJG system. One can see that the anomaly is very pronounced for the temperature $T = 0.15$, but it rapidly disappears with increasing temperature. At $T = 0.3$ the anomaly is already of the order of numerical accuracy and we estimate this temperature as the temperature where viscosity anomaly disappears.

The location of diffusion, density and structural anomalies of LJG system in $\rho - T$ plane have already been reported in literature [12]. Figs. 2 shows the re-

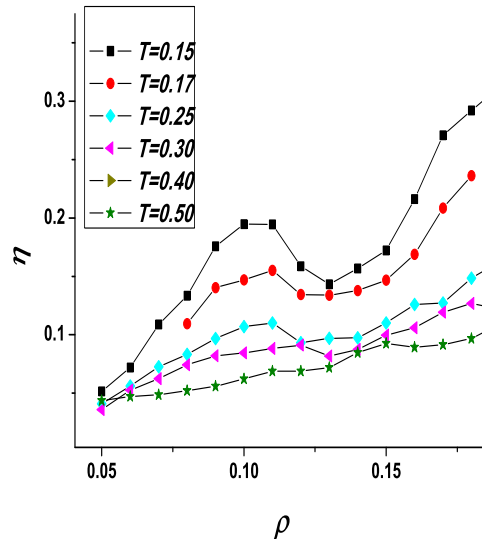


FIG. 1: (Color online). Viscosity anomaly in LJG system.

gions of these anomalies and the viscosity anomaly. Interestingly, as it was proposed in Ref. [22] the anomalous regions are enveloped in each other. However, the viscosity anomaly violates this rule: it has partial overlap with density anomaly, but no one of them is inside of one another. It was also shown in the literature that from the thermodynamic arguing it follows that the density anomaly region is always inside the structural anomaly one, while the diffusion anomaly can have any location with respect to the other anomalies [5, 23]. The viscosity anomaly is another example of anomalies of dynamic rather than thermodynamic properties. Therefore, one can expect that the viscosity anomaly can also have any possible location with respect to the density and structure anomalies.

In our previous work we showed that the anomalies can be visible along some paths in thermodynamic space while along others they can be invisible [13–15]. For example, diffusion anomaly is seen along isotherms but not isochors. An important consequence of this difference is that Rosenfeld excess entropy scaling for diffusion coefficient [24, 25] is fulfilled along isochors but breaks down along isotherms [18]. This makes important to see the viscosity behavior along different trajectories.

Figs. 3 shows shear viscosity of LJG system along several isochors. One can see that viscosity demonstrates a minimum. Viscosity minimum along isobars was observed experimentally for water [20]. The authors called this minimum as "viscosity anomaly". However, in our previous work we showed that viscosity minimum along isochors appears naturally because of the interplay of potential-potential and kinetic-kinetic correlations even in simple liquids [21]. The same results can be obtained

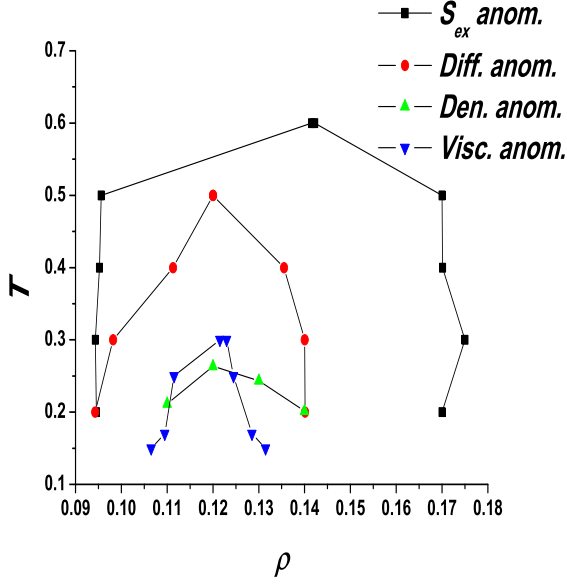


FIG. 2: (Color online). Location of anomalous regions in ρ - T plane for LJG system.

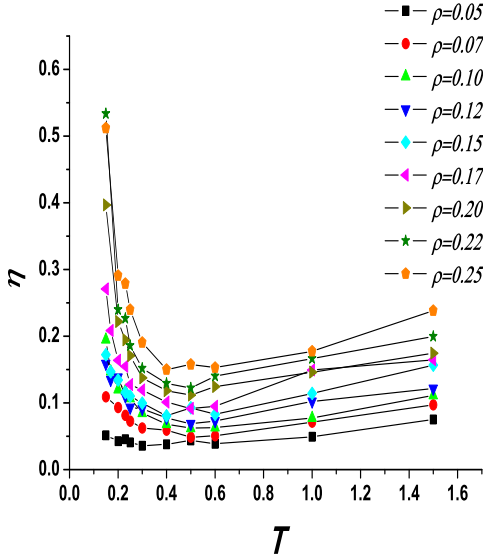


FIG. 3: (Color online). Shear viscosity of LJG system along several isochors.

for isobars (not shown in Ref. [21]).

Figs. 4 shows the Rosenfeld relation for shear viscosity of LJG system along isochors. One can see that the linear relation between $\ln(\frac{\eta\rho^{-2/3}}{T^{1/2}})$, which is predicted by Rosenfeld relation, holds true except the low S_{ex} region. However, if we consider the Rosenfeld relation along isotherms we see that it breaks down at low temperature (Figs. 5 (a)). Here we observe a self crossing loop like the one observed for diffusion in our previous works [13–15, 18].

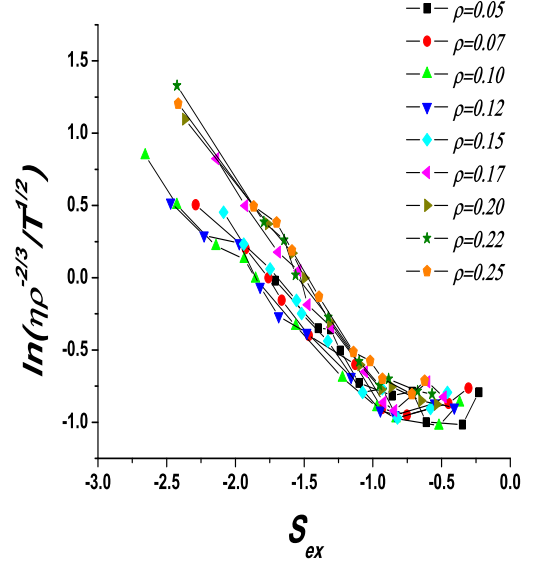


FIG. 4: (Color online). Rosenfeld relation for shear viscosity of LJG system along isochors.

Fig. 5 (b) shows the Rosenfeld scaling for high temperature ($T = 1.0$). Points correspond to the data from simulations while the straight line is the best fit line. One can see that the simulation points demonstrate some kind of oscillations around the best fit line. We relate these oscillations to the numerical inaccuracies in the viscosity computations and we believe that Rosenfeld scaling of viscosity does work for high enough temperatures.

One can conclude that as in the case of diffusion coefficient Rosenfeld relation for shear viscosity in systems with thermodynamic anomalies holds true along isochors but breaks down along low temperature isotherms. This confirms the idea of different behavior of a system along different trajectories in ρ - T - P space which is discussed in details in Ref. [14, 15].

Soft Repulsive Shoulder system

The second system considered in this work is Soft Repulsive Shoulder System (Eq. (2)). Phase diagram and anomalous behavior of this system were studied in details in our previous works [16–18]. However, the shear viscosity of this system is measured for the first time.

Figs. 6 (a) and (b) show the shear viscosity of SRSS system along several isotherms. One can see that at the lowest temperature $T = 0.15$ a tiny loop develops at the densities $\rho = 0.40 - 0.45$. However, the size of this loop is inside the error bar, so we can not consider it as a real anomaly. We believe that the anomaly appears at lower temperatures. Though the shear stress autocorrelation function decays very slowly and viscosity calculations be-

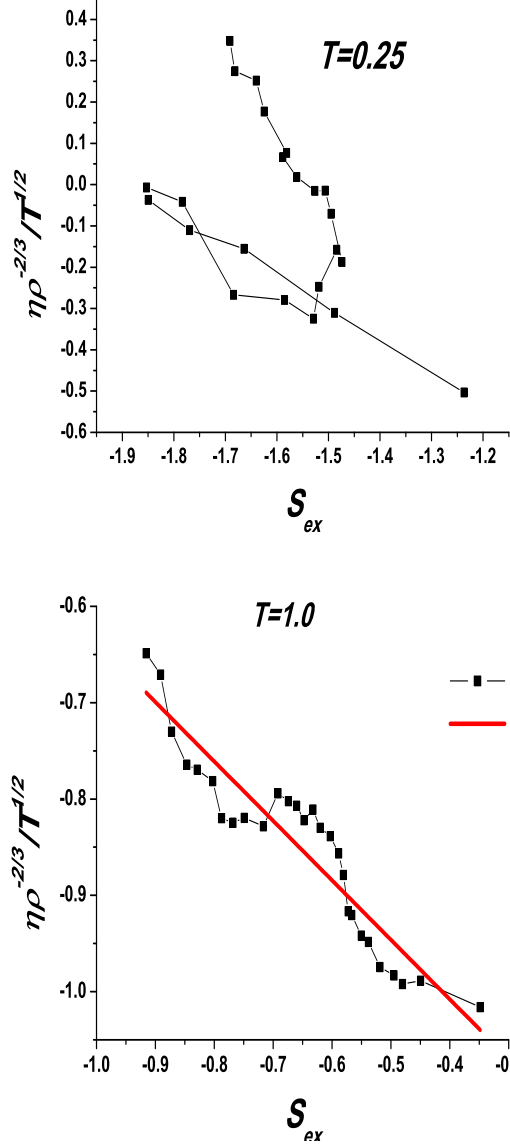


FIG. 5: (Color online). Rosenfeld relation for shear viscosity of LJG system along isotherms at low and high temperature.

come very difficult.

Figs. 7 shows the shear viscosity plotted along a set of isochors. One can see that for all presented densities the viscosity curves monotonically decrease with increasing temperatures. Basing on the arguments of our previous work [21] we expect that shear viscosity passes a minimum at higher temperatures.

Figs. 8 (a) and (b) show the Rosenfeld scaling plots for SRSS along isotherms and isochors. One can see that the scaling relations break down in case of isotherms. The reason for this breakdown is that while viscosity is monotonous function of density the excess entropy demonstrates anomalous behavior [14, 15]. As a result

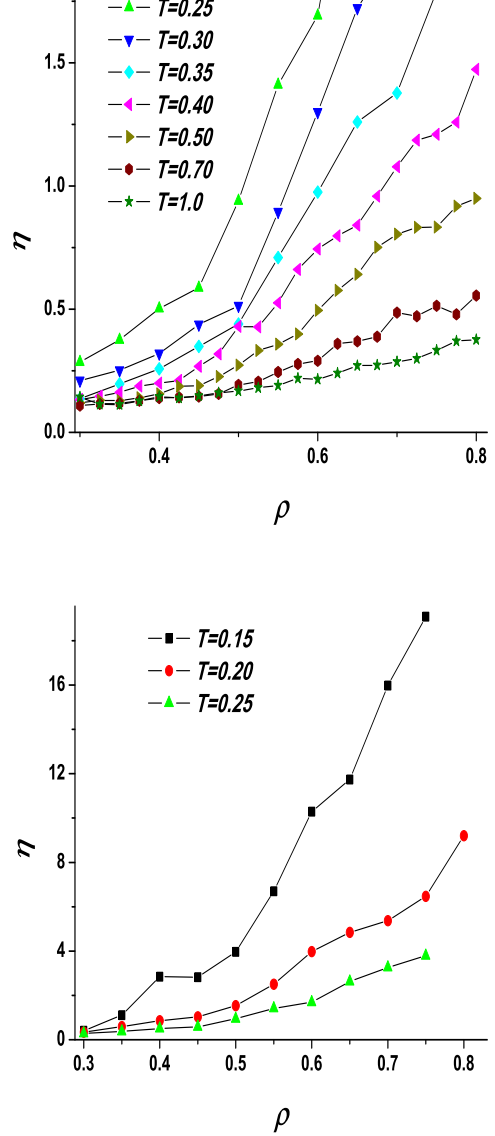


FIG. 6: (Color online). Viscosity of SRSS system along a set of isotherms at (a) low and (b) intermediate and high temperatures.

viscosity as function of S_{ex} demonstrates nonlinear behavior.

At the same time Rosenfeld relation holds true along isochors (Figs. 8 (b)). All isochors can be divided in low ($\rho \leq 0.45$) and high density ($\rho > 0.45$) groups. The curves belonging to the same groups have similar slopes while the slope of the curves from different groups is essentially different. The reason for this change is that at low densities the system can be essentially approximated by the system with effective diameter σ while at high densities with diameter d . This change of particle size alters also the kinetic and thermodynamic proper-

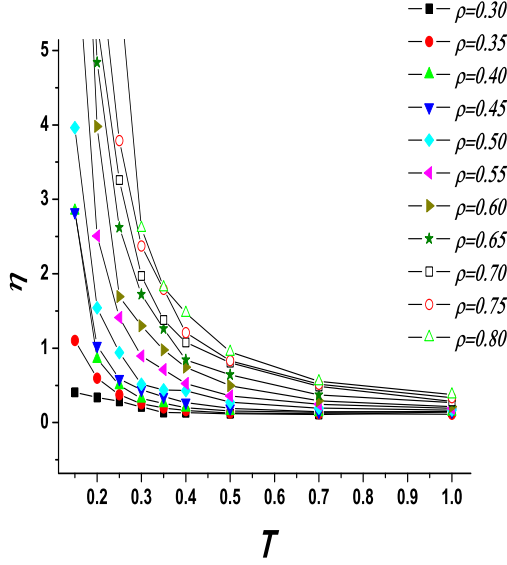


FIG. 7: (Color online). Viscosity of SRS system along a set of isochors.

ties of the system which we observe as the slope change in Figs. 8 (b).

Stokes-Einstein Relation

In our previous work [14, 15] we showed that the discrepancy in the diffusion and structural anomalies regions leads to the Rosenfeld relation breakdown along isotherms. As it was shown in the previous section the regions of diffusion and viscosity anomalies are also different. In this respect it becomes important to see if Stokes-Einstein relation still holds true in the anomalous regions.

The Stokes-Einstein relation can be written in the following form:

$$c_{SE} = \frac{k_B T}{\pi D \eta d} \approx const, \quad (3)$$

where d is the character particle size. The coefficient c_{SE} should be approximately constant and belong to the interval $2 \leq c_{SE} \leq 3$. The limiting values $c_{SE} = 2$ and $c_{SE} = 3$ correspond to the stick and slip boundary conditions.

Figs. 9 (a) and (b) show the Stokes-Einstein coefficient for LJG and SRSS systems along isochors. One can see that in both cases c_{SE} is not constant. At the same time the numerical values of c_{SE} in both cases can be far from the interval $[2, 3]$. In our previous work we studied Stokes-Einstein relation for Soft Spheres system [26]. It was found that Stokes-Einstein relation can be fulfilled

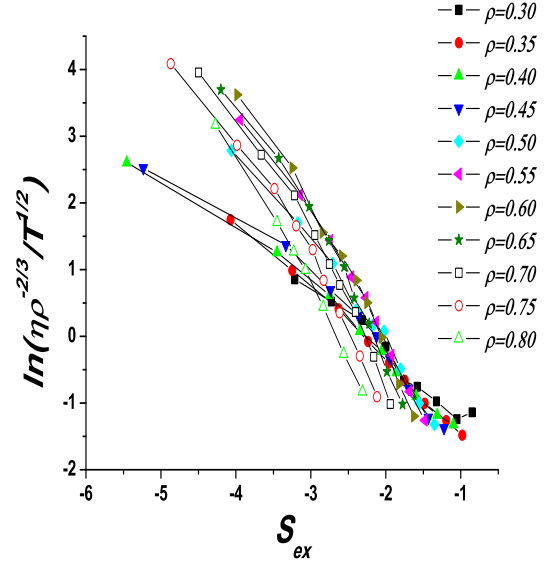
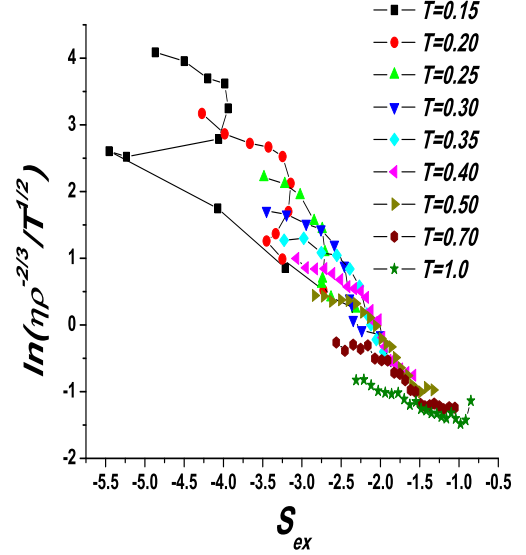


FIG. 8: (Color online). Rosenfeld scaling plots for SRS along (a) isotherms and (b) isochors.

there if one takes the effective particle diameter as Barker perturbation theory one $d \sim T^{-1/n}$, where n is the softness coefficient. However, in the case of core-softened systems the situation is more complicated. These systems have two character length scales and the applicability of perturbation theory to such systems is questionable.

From figs. 9 (a) and (b) one can see that the qualitative behavior of c_{SE} is defined by the viscosity behavior. For example, the maximum of c_{SE} appears at the temperatures of minimum of viscosity. At the same time viscosity of SRSS is monotonous and we observe that c_{SE} is also monotonous in this case. However, one needs more detailed investigations to give any conclusive statements on

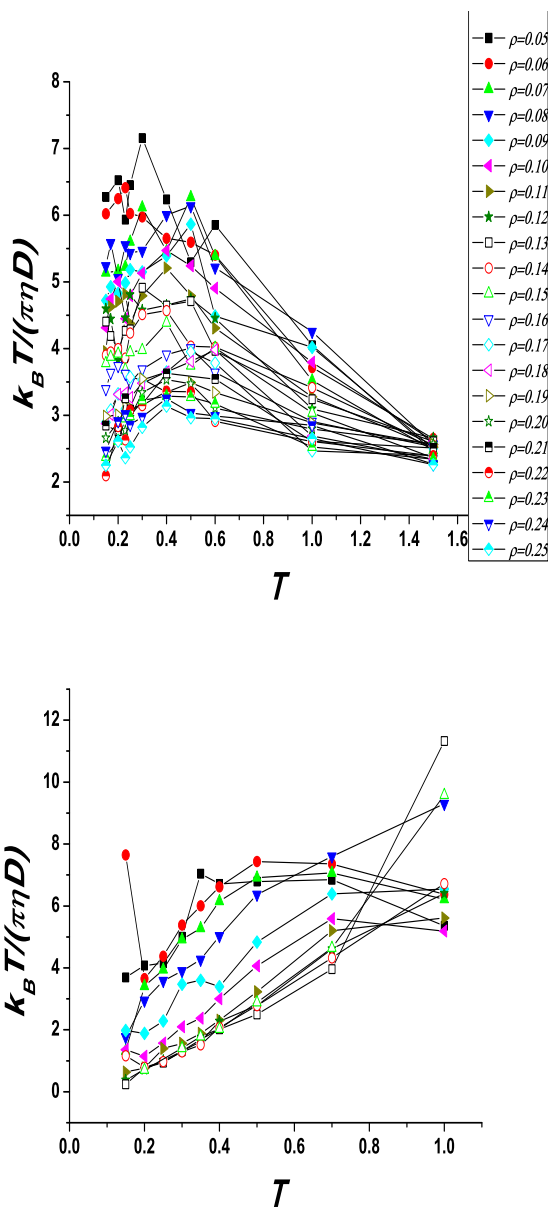


FIG. 9: (Color online). c_{SE} for (a) LJG system and (b) SRS along several isochores.

Stockes-Einstein relation for core-softened systems.

CONCLUSIONS

It is well known from the literature that many core-softened liquids demonstrate some kind of anomalies. One of the typical anomalies in the core-softened systems is diffusion anomaly. It is also widely believed that diffusion is strongly connected to shear viscosity by Stockes-Einstein relation. In this respect it is interesting to see if the same systems demonstrate viscosity anomaly as well. In the present work we investigate this question.

We find that the viscosity anomaly does exist, however, the region of $(\rho - T)$ parameters where viscosity demonstrate anomalous behavior is different from the diffusion anomaly region. We place the regions of different anomalies in the same plot to see the relations between them. Finally we check the Stockes-Einstein relation for the liquids under investigation.

We thank S. M. Stishov, E. E. Tareyeva and V.V. Brazhkin for stimulating discussions. Y.F. thanks the Joint Supercomputing Center of the Russian Academy of Sciences for computational power and the Russian Scientific Center Kurchatov Institute for computational facilities. The work was supported in part by the Russian Foundation for Basic Research (Grants No 13-02-00913, No 11-02-00341-a and No 13-02-00579) the Ministry of Education and Science of Russian Federation (projects 8370, 8512, Scientific School No 5365.2012.2 and Young Candidates Grant No 2099.2013.2).

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